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TITLE: VIBRATIONAL SPECTROSCOPY OF SHOCK-COMPRESSED FLUID N_2 AND O_2

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VIBRATIONAL SPECTROSCOPY OF SHOCK-COMPRESSED FLUID N_2 AND O_2 *

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Single-pulse multiplex coherent anti-Stokes Raman scattering (CARS) was used to observe the vibrational spectra of liquid N_2 shock-compressed to several pressures and temperatures up to 41 GPa and 5200 K and liquid O_2 shock-compressed to several pressures and temperatures up to 10 GPa and 1000 K. For N_2 , the experimental spectra were compared to synthetic spectra calculated using a semi-classical model for CARS intensities and estimated vibrational frequencies, peak Raman susceptibilities, and Raman line widths. The question of excited state populations in the shock-compressed state is addressed.

Recently the high-pressure, high-temperature behavior of N_2 and O_2 has received considerable attention. Several dynamic [1-7] and static [8-16] experiments have produced equation of state and thermodynamic data for N_2 at pressures up to 130 GPa and at elevated temperatures to beyond 10,000 K and for O_2 at pressures up to 140 GPa and to temperatures beyond 10,000 K. These measurements have been complemented by calculations which describe the thermodynamic state of the solid [17,18] or the fluid [19-23]. An increase in compressibility along the N_2 Hugoniot at pressures above 30 GPa has been attributed [18,19,23] to dissociation. The intramolecular stretching frequencies for solid N_2 [12,24,25] and solid O_2 [13,26-28] have been measured and calculated [29,30] using a perturbation analysis in conjunction with appropriately chosen intra- and intermolecular potential functions [22,23]. Vibrational frequencies have also been measured for the fundamental and some excited-state transitions of fluid N_2 at pressures and

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temperatures up to 34 GPa and 4400 K [11,31]. Recently Monte Carlo techniques [32] and a model based on a sphericalized potential [33], have been used to calculate the N_2 vibrational frequency at pressures and temperatures up to 34 GPa and 4400 K respectively. There have, however, been no measurements or calculations of O_2 vibrational frequencies in the dense-fluid state. Such results and higher pressure/temperature data for N_2 would be of value both to characterize the intramolecular potential functions of these molecules and possibly to verify directly the existence of dissociation. Measurements of ground- and excited-state vibrational-transition intensities could also provide an upper limit estimate for dense-phase fluid-vibrational relaxation times [34,35].

Reported here are coherent anti-Stokes Raman scattering (CARS) measurements for N_2 and O_2 shock-compressed to 41 GPa and 10 GPa, respectively. The pressure, temperature states were achieved by dynamic compression techniques using an experimental apparatus described previously [36,37]. Briefly, a projectile launched by a two-stage light-gas gun dynamically compressed a liquid N_2 or O_2 sample that had been condensed in a cryogenic target assembly. The target was designed to reflect the CARS signal from a highly polished 304 stainless steel target plate at the front through a 6.3-mm-diam quartz or lithium fluoride window at the rear. Impactor and target plate thicknesses were chosen, and pin assemblies were installed in the ~1.5-mm-long liquid sample, so as to insure that rarefaction waves would not compromise the one-dimensional character of the compression in the region observed optically. Single shock velocities were conservatively measured to ± 0.2 km/s and the initial pressure and temperature of the liquid sample were determined to ± 0.1 GPa and ± 1 K respectively. Initial sample densities of N_2 and O_2 were taken from Jacobsen, et al. [38] and Weber [39], respectively. The samples were condensed from gaseous N_2 (purity greater than 99.9%) and gaseous O_2 (purity greater than 99.6%).

A Nd:YAG laser was used to pump the two dye lasers used to generate the CARS signal. The laser dye DCM was used in the broadband dye laser to produce Stokes frequencies from 630 nm to 650 nm. The pump frequency in the CARS process was

obtained by using approximately 40% of the Nd:YAG laser output to pump a narrow-band dye laser (Quanta-Ray PDL-1) at near 557 nm for N_2 experiments and near 582 nm for O_2 experiments. Multi-channel detection of the CARS signals was done using an intensified photodiode array (Tracor Northern Model 6132) and analyzer (Tracor Northern Model 6500). In addition, the broadband dye laser spectral profile was measured in each experiment using another one-meter spectrometer, and either a photodiode array (Reticon Model RL512S) and a transient digitizer (Biomation Model 805) or a Princeton Instruments OSMA System.

Pressures and temperatures, as given in Figs. 1 and 2 for the singly and doubly shocked regions, were calculated using an effective spherical potential [22,23] that has been shown to reproduce accurately both nonspherical molecular dynamics simulations and experimental Hugoniot and brightness temperature data for N_2 . Taking into account the accuracy of the method for N_2 , and the similarity of potentials for N_2 and O_2 an effective spherical potential for O_2 was fit directly [7] to Hugoniot data [6] and was checked by its good fit to reflected shock data [6]. In this work, doubly-shocked states are inferred from impedance matching of the initial shock, at the measured shock velocity, reflecting off the known window material assuming the theoretical equation of state for N_2 or O_2 . The equation of state parameters for quartz and lithium fluoride are from published data [40]. Based on the previously stated experimental errors, estimated uncertainties in pressure are about ± 1 GPa for principal Hugoniot measurements and ± 2 GPa for reflected shocks. These uncertainties are dominated by the experimental uncertainty in the shock velocity. Temperature uncertainties are dominated by a systematic shift of up to 10 percent depending on the theoretical model chosen [17,20].

CARS [41-46] occurs as a four-wave parametric process in which three waves, two at a pump frequency, ω_p , and one at a Stokes frequency, ω_s , are mixed in a sample to produce a coherent beam at the anti-Stokes frequency, $\omega_{as} = 2\omega_p - \omega_s$. The efficiency of this mixing is greatly enhanced if the frequency difference,

$\omega_p - \omega_s$, coincides with the frequency of a Raman active mode of the sample. The intensity of the beam at ω_{as} is given by

$$I_{as} = \sum_i \frac{\omega_{as}^2 I_p^2 I_s (N_i L_i)^2}{n_p^2 n_s n_{as}} \left(\frac{n_{as}^2 + 2}{3} \right)^2 \left(\frac{n_s^2 + 2}{3} \right)^2 \left(\frac{n_p^2 + 2}{3} \right)^4$$

$$\times \left[\left(\sum_j \frac{\Gamma_j \chi_j^{pk} (\omega_j - \omega_p + \omega_s)}{(\omega_j - \omega_p + \omega_s)^2 + \Gamma_j^2} + \chi^{NR} \right)^2 + \left(\sum_j \frac{\Gamma_j^2 \chi_j^{pk}}{(\omega_j - \omega_p + \omega_s)^2 + \Gamma_j^2} \right)^2 \right] \quad (1)$$

and

$$\Gamma_j \chi_j^{pk} \frac{h}{2\pi c} \omega_p \omega_s^3 = \left(\frac{d\sigma}{d\Omega} \right)_j (\rho_j - \rho_k) \quad (2)$$

where h is Planck's constant, c is the speed of light, and n_{as} , n_s , and n_p are the refractive indices at ω_{as} , ω_s , and ω_p , respectively. I_p and I_s are the incident intensities of the pump and Stokes beams respectively. $N_i L_i$ corresponds to the Lagrangian density of the i th layer, and the sum is over non-interfering layers. χ^{NR} is the non-resonant susceptibility, χ_j^{pk} is the peak third order susceptibility, Γ_j is the half width at half maximum (HWHM) linewidth, and $(d\sigma/d\Omega)_j$ is the spontaneous Raman cross-section of the j -to- k vibrational transition. ρ_j is the number density in vibrational level j . The sum on j 's over transitions. Equations (1) and (2) hold only in the case of no electronic resonance enhancement [42].

Phase-matching is assumed to be experimentally optimized in the ambient sample for the focusing conditions used. The dispersion in the N_2 sample is assumed to scale linearly with the increase in refractive index due to volume compression according to the empirical relation $n = 1.22 + 0.52(1-V/V_0)$ [47]. V/V_0 is the relative volume due to compression and 1.22 is the approximate index of refraction of ambient liquid N_2 [48,49]. Linear scaling of the dispersion results in the same phase-matching angle at all compressions. These refractive

into the local field correction terms of Eq. (1).

Wavelength calibrations ($\pm 2 \text{ cm}^{-1}$) were all done using vacuum wavelengths of atomic emission lines [50]. For the N_2 experiments, the narrowband dye laser was placed near or in coincidence with the 17947.4 cm^{-1} transition of Kr. The intensified-diode array that detects CARS signals was calibrated using either the 19931.9 cm^{-1} and 20311.6 cm^{-1} transitions of He and the 19844.6 cm^{-1} transition of Ne, or the 19882.0 cm^{-1} and 20641.3 cm^{-1} transitions of Xe. For the O_2 experiments, the narrowband dye laser was placed in coincidence with the 17176.9 cm^{-1} transition of Ne, and the intensified-diode array was calibrated using the 18753.8 cm^{-1} and 18511.4 cm^{-1} transitions of Ne. For both sets of experiments, the broadband-dye-laser spectral profile was calibrated against either the 15615.2 cm^{-1} and 15662.3 cm^{-1} or 15782.4 cm^{-1} and 15364.9 cm^{-1} transitions of Ne. The spectral slit function of the spectrometer/intensified-diode-array combination was measured using the 19931.9 cm^{-1} line of He and an $100\text{-}\mu\text{m}$ -wide entrance slit. A good representation of this slit function was obtained by use of a 2.9 cm^{-1} FWHM triangle. The spectral profile of the narrowband laser was accurately measured and was fit best by a Gaussian with 1.3-cm^{-1} width at $1/e$ -amplitude.

The observed single-pulse CARS spectra of ambient pressure and eight (four experiments) dynamically-compressed states of liquid nitrogen are shown in Fig. 1. Also shown are preliminary calculations of synthetic spectra made using Eq. (1). Because of timing constraints and the desire to have no unshocked sample at the time the laser pulses arrived, the shockwave in the experiments has reflected off of the rear window back into the once-shock-compressed sample, producing a doubly-shocked region. Because the ambient liquid N_2 Raman linewidth is sufficiently narrow [51-53] and because the line broadening with pressure is observed here to be sufficiently slow, spectral features from both the singly- (denoted in Fig. 1 by asterisks) and doubly- (arrows) shocked regions are clearly observed.

Previous observations by Reichlin, et al. [12] for solid N_2 show that the vibrational frequencies tend to first increase and then decrease with increasing pressure. Visual inspection of the data in Fig. 1 suggests this same phenomenon may also occur at Hugoniot conditions, only with the reversal occurring at much lower pressures. This behavior has been suggested by the calculations of Etters, et al. [32] and LeSar [33]. The data are presently being analyzed using techniques discussed previously [31] to obtain more accurate values for transition frequencies, peak Raman susceptibilities, and Raman line widths.

Experimental results [34,35,54,55] show that the dense-fluid- N_2 vibrational-relaxation time decreases from greater than 7 s at atmospheric pressure to approximately 0.2 ms at 0.3 GPa. Because these times are long it is unclear whether, for the shock pressures and temperatures shown in Fig. 1, the relaxation time will decrease sufficiently rapidly (to ≈ 50 ns) to enable equilibration of the vibrational levels in the shock-compressed region interrogated by CARS. It is also unclear what effect impurities will have on the density dependence of the relaxation time [34,35]. Ratios of Eq. (2) for excited-state to fundamental-transitions for the lower pressure data [31] were used to explore the possibility of a non-Boltzmann population distribution for the excited states. The right-hand-side ratios were calculated using the harmonic oscillator approximation for the variation of the Raman cross section with vibrational level, $(d\sigma/d\Omega)_j \propto (j+1)$, and assuming a Boltzmann distribution for ρ_j . For these transitions, the ratios of the left side determined using previous experimental values [31] agreed with the values calculated for the right-hand side. This suggests that, subject to the stated approximations, vibrational equilibration occurs faster than 50 ns at these pressures and temperatures. However, because of the large uncertainties in the experimental quantities [31], particularly the peak third-order susceptibilities and the Raman half-widths, this conclusion does not yet merit a definite statement. We are presently doing similar calculations for the higher-pressure data.

The observed single-pulse CARS spectra of ambient pressure and five (four experiments) dynamically-compressed states of liquid oxygen are shown in Fig. 2. For the higher-pressure data in these experiments, the shock wave had not reached the rear window of the target assembly. Hence only the singly-shocked (asterisks) and ambient-pressure (unlabeled) states are observed spectrally. We are presently analyzing these data using the semiclassical model, Eq. (1), for CARS intensities. Because a possible absorption [26,27,56], due to either a van der Waals interaction-induced or a collisionally-induced transition at the frequencies of the CARS lasers, could dramatically influence the third-order susceptibility in Eq. (1) [45], it is first necessary to perform an absorption experiment at the pressures and temperatures of interest. Such measurements are in progress. A visual inspection of the data, however, suggests that, similar to the N_2 results given in Fig. 1, a nonlinear increase with pressure is also evident for the O_2 0-1 transition frequency.

In summary, the observation of vibrational transitions of the N_2 and O_2 , at pressures up to 41 GPa (5200 K) and 10 GPa (1000 K) respectively, suggests that at these conditions, N_2 and O_2 still exist as molecular fluids. Visual inspection of the N_2 and O_2 spectral data suggests that for both molecules the vibrational frequencies initially increase with increasing pressure along the Hugoniot, but at higher pressures this trend is reversed. This would indicate first a narrowing and then a broadening of the intramolecular potential function. Also, higher vibrational states in N_2 are excited in <50 ns. Within the limits of the approximations used and the experimental error, thermal equilibration of these levels is suggested.

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FIGURE CAPTIONS

Figure 1. Experimental and computed spectra for high pressure and temperature N_2 .

Figure 2. Experimental spectra for high pressure and temperature O_2 .



